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An Electrolyte for Low-Temperature Applications of Lithium and Lithium-Ion Batteries

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An Electrolyte for Low-Temperature Applications of Lithium and Lithium-Ion Batteries

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Abstract

An electrolyte consisting of a 1.0-molar solution of lithium hexafluorophosphate ($LiPF_6$) in 1:1:1 ethylene carbonate (EC)-dimethyl carbonate (DMC)-ethyl methyl carbonate (EMC) is proposed for low-temperature applications. The new electrolyte has good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to –40 °C.

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Introduction

Various Army missions require lithium and lithium-ion batteries that can operate at temperatures down to –40 °C. Because the electrolytes presently used in commercial lithium-ion batteries freeze at about –30 °C, considerable attention is being given to finding cosolvents for these electrolytes to increase their liquidus range. Recently, ethyl methyl carbonate (EMC) was found to be a useful cosolvent[1–3] in binary solutions with propylene carbonate (PC) and ethylene carbonate (EC), because of its low freezing point (–55 °C). In this study, we used EMC as a cosolvent with EC and dimethyl carbonate (DMC) in ternary solutions to increase the liquidus range of the lithium-ion battery electrolyte. Thus, $Li/LiCoO_2$ and graphite/$LiCoO_2$ button cells that use a 1.0-molar solution of lithium hexafluorophosphate ($LiPF_6$) in 1:1:1 EC-DMC-EMC as the electrolyte were found to be operable at temperatures down to –40 °C. Further, the new electrolyte was found to have good conductivity, as well as good electrochemical stability. The results are summarized in this report.

Experimental Procedure

$LiPF_6$ (from Hashimoto, Japan) and SFG-44 graphite (from Timcal) were used as received. EC, DMC, and EMC (all from Grant Chemicals) were dried over molecular sieves before use. Lithium foil (20 mil thick, from the Cypress-Foote Mineral Company), packed over argon, was opened in an argon-filled dry box (from the Vacuum Atmosphere Company) with a moisture content of less than 0.5 ppm.

The electrolyte conductivities were measured with a Wayne Kerr model 6425 precision bridge at a frequency of 1 kHz in sealed Jones-type conductivity cells. Cell constants were determined by a standard KCl solution. An environmental chamber (manufactured by Tenney, Jr.) controlled the temperature for the conductivity and cell studies.

We fabricated lithium and lithium-ion cells using a 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC in a button cell configuration. The cell component specifications and button cell assembly details have been described previously.[4] All electrode disks were 0.51 mm thick and 15.7 mm in diameter. Lithium electrodes were cut from a lithium foil and pressed onto nickel screen (Exmet 5 Ni 6-3/0A). Graphite electrodes with a theoretical capacity of 24 mAh were fabricated with the use of 10 wt.%

[1] *M. Ue and S. Mori, "Mobility and ionic association of lithium salts in propylene carbonate-ethyl methyl carbonate mixed solvents," J. Electrochem. Soc.* ***142****, 2577 (1995).*

[2] *Y. Ein-Eli, S. R. Thomas, V. Koch, D. Aurbach, B. Markovsky, and A. Schechter, "Ethylmethylcarbonate, a promising solvent for Li-ion rechargeable batteries," J. Electrochem. Soc.* ***143****, L273 (1996).*

[3] *Y. Ein-Eli and V. R. Koch, "Li-ion battery electrolytes formulated for low temperature applications," Proceedings of the Workshop for Battery Exploratory Development, pp 253–259, Burlington, VT (July 1997).*

[4] *E. J. Plichta and S. Slane, "Conductivity of lithium imide in mixed aprotic solvents for lithium cells," J. Power Sources* ***69****, 41 (1997).*

PTFE (Teflon) binder. The electrode mixture was spread on a copper foil current collector. We made lithium cobalt oxide electrodes with a theoretical capacity of 42 mAh by mixing 80 wt.% $LiCoO_2$ with 10 wt.% Vulcan CX-72R carbon and 10 wt.% PTFE and spreading the paste on an aluminum screen current collector. The cells were fabricated with a Celgard 2402 separator (0.05 mm thick and 1.9 cm in diameter). The cells were cycled by an Amel model 546 galvanostat/electrometer, and the currents applied to the cell were verified with a Fluke model 8640A digital multimeter. We performed voltammetric scans using an EG&G PAR potentiostat/galvanostat (model 273). The experiments were computer-controlled with the use of EG&G PAR electrochemical analysis software (model 270).

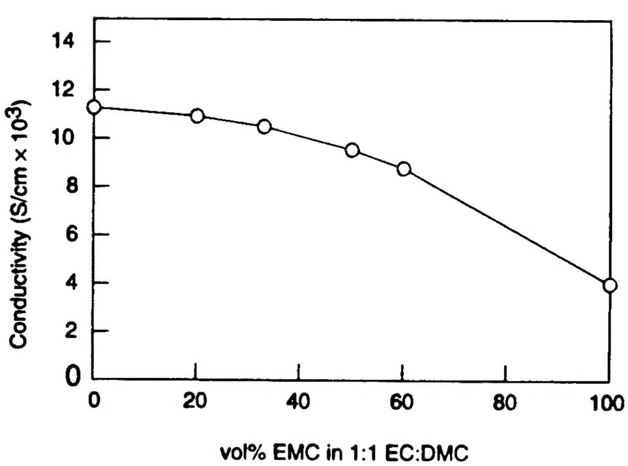
Results and Discussion

The electrolyte in commercial lithium-ion cells generally consists of a 1.0-molar solution of $LiPF_6$ in 1:1 EC-DMC (50:50 vol.%). The electrolyte freezes at about –30 °C, so the commercial lithium-ion cells cannot be used in several military applications that require operation at lower temperatures. We have, therefore, employed EMC as a cosolvent to increase the liquidus range of the electrolyte used in commercial cells.

The conductivities of 1.0-molar solutions of $LiPF_6$ in 1:1 EC-DMC containing 0 to 100 vol.% EMC were measured at 25 °C, and the data are plotted in figure 1. It is seen that the electrolyte conductivity decreases from ~0.011 to ~0.004 S/cm as the concentration of EMC is increased from 0 to 100 vol.%. However, the decrease in electrolyte conductivity is only minimal in the initial stages, and the conductivity of a 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC is close to the conductivity in a 1:1 EC-DMC solution.

We found the freezing point of a 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC to be approximately –50 °C compared to the freezing point of approximately –30 °C for the electrolyte using a 1:1 EC-DMC, binary solvent mixture. The conductivities of 1.0-molar solutions of $LiPF_6$ in EMC, 1:1 EC-DMC, and 1:1:1 EC-DMC-EMC were also measured in the

Figure 1. Conductivities of 1.0-molar solutions of $LiPF_6$ in ternary solvent mixture EC-DMC-EMC as function of percentage volume of EMC at 25 °C.



temperature range of –40 °C to 55 °C. The data are plotted in figure 2 as a function of temperature.

The conductivities of the EMC solutions at all temperatures are too low to consider these solutions as electrolytes for lithium or lithium-ion batteries. However, EMC can be used as a cosolvent for the commercial electrolyte consisting of a 1.0-molar solution of $LiPF_6$ in 1:1 EC-DMC to increase its liquidus range. The conductivities of the electrolyte using the ternary solvent mixture are, however, slightly lower at temperatures above –20 °C (fig. 2) compared to the conductivities of electrolytes using the binary solvent mixture.

The electrochemical stabilities of solutions of $LiPF_6$ in EMC, 1:1 EC-DMC, and 1:1:1 EC-DMC-EMC were examined by recording linear sweep voltammograms at smooth glassy carbon electrodes (electrode area: 0.0792 cm^2). Typical voltammograms obtained at a scan rate of 20 mV/s are presented in figure 3. It is seen that all three solutions are electrochemically stable up to a potential of about 4.5 V, although the anodic currents in EMC solutions are much smaller than those observed in the EC-DMC and EC-DMC-EMC solutions.

Figure 2. Conductivities of 1.0-molar solutions of $LiPF_6$ in EMC (△), 1:1 EC-DMC (○), and 1:1:1 EC-DMC-EMC (□) as function of temperature.

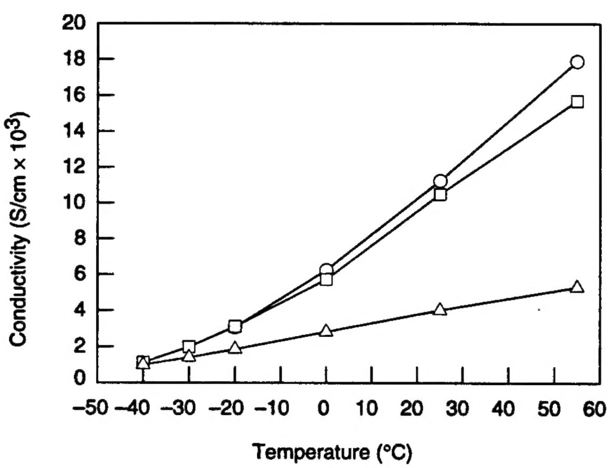
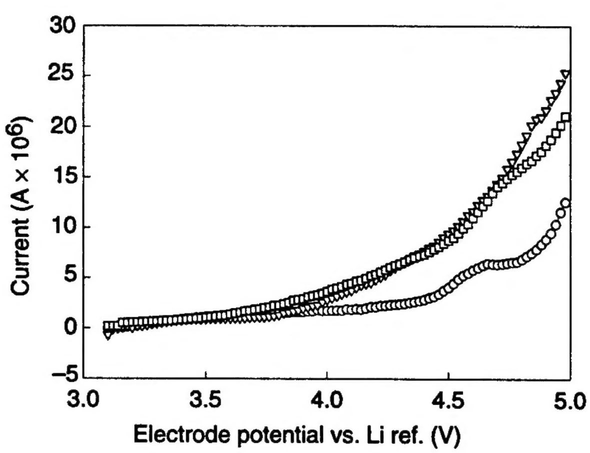


Figure 3. Linear sweep voltammograms obtained at glassy carbon electrode at scan rate of 20 mV/s in 1.0-molar solutions of $LiPF_6$ in EMC (○), 1:1 EC-DMC (△), and 1:1:1 EC-DMC-EMC (□).



The new electrolyte was evaluated in the following cells:

Li/electrolyte/SFG-44 graphite (I)

Li/electrolyte/$LiCoO_2$ (II)

SFG-44 graphite/electrolyte/$LiCoO_2$ (III)

Cell I was used to determine the reversible and irreversible capacity of the graphite electrode in button cells. The cell was discharged at a constant current of 1 mA to 0.01 V, which resulted in the intercalation of lithium into graphite. The total cell reaction may be represented as

$$x\,\mathrm{Li} + 6\mathrm{C} \leftrightarrow \mathrm{Li}_x\mathrm{C}_6 \quad (1)$$

The cell was then cycled between the voltage limits of 0.01 and 1.5 V, and the voltage-time plots for the first discharge and the following charge-discharge cycle are shown in figure 4. This plot is similar to plots observed by other workers for lithium/graphite cells using nonaqueous electrolytes.[3,5] The capacities of the graphite electrode during the initial discharge and the following charge-discharge cycle were found to be 354.4, 322.7, and 323.9 mAh/g, respectively. Thus, the irreversible capacity during the first discharge was ~31.7 mAh/g. After the initial discharge, the capacity of the graphite electrode was found to be approximately the same for the charge and discharge cycles.

The reversible capacity of ~323 mAh/g for the graphite electrode was found to be comparable to the capacity reported by other workers[5] for graphite electrodes.

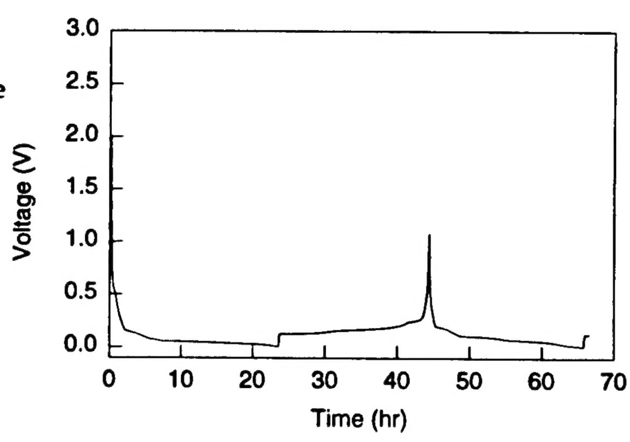


Figure 4. Typical voltage-time curve for cell I for first discharge and following charge-discharge cycle at constant current of 1 mA using 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC as electrolyte.

[3]*Y. Ein-Eli and V. R. Koch, "Li-ion battery electrolytes formulated for low temperature applications," Proceedings of the Workshop for Battery Exploratory Development, pp 253–259, Burlington, VT, July 1997.*

[5]*S. Megahed and B. Scrosati, "Lithium-ion rechargeable batteries," J. Power Sources* **51**, *79 (1994).*

Cells II and III were used to study the performance of the lithium and lithium-ion cells at different temperatures using a 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC as the new electrolyte. The cell reactions in cells II and III, respectively, may be represented as

$$x\,Li + Li_{1-x}CoO_2 \leftrightarrow LiCoO_2\text{, and} \tag{2}$$

$$Li_xC_6 + Li_{1-x}CoO_2 \leftrightarrow 6C + LiCoO_2\ . \tag{3}$$

Both cells II and III were assembled in the discharged state and were first charged to a voltage of 4.15 V at a constant current of 1 mA. The discharge curves obtained at 25 °C, –20 °C, and –40 °C at a constant discharge current of 1 mA for cells II and III are presented in figures 5 and 6.

It can be seen that both cells II and III are operable at temperatures down to –40 °C. The capacity of the lithium-ion cell (fig. 6) at –40 °C was, however, found to be only a fraction of the capacity obtained at 25 °C. This may be attributed to the poor performance of the graphite-lithium anode at –40 °C, since the capacity of the lithium cell (fig. 5) at the same temperature was found to be about 52 percent of the capacity obtained at 25 °C.

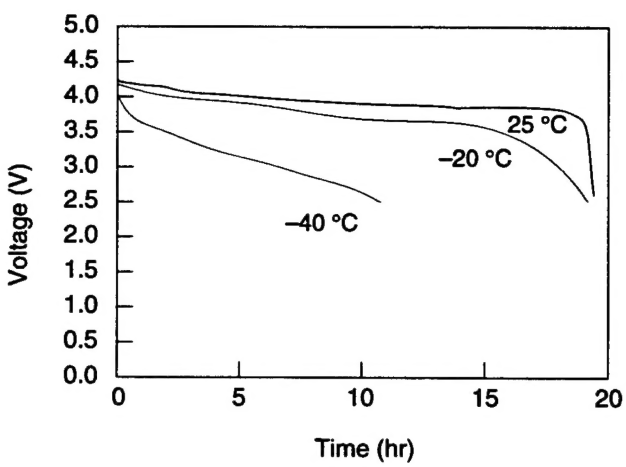


Figure 5. Typical discharge curves for cell II at constant current of 1 mA at various temperatures using 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC as electrolyte.

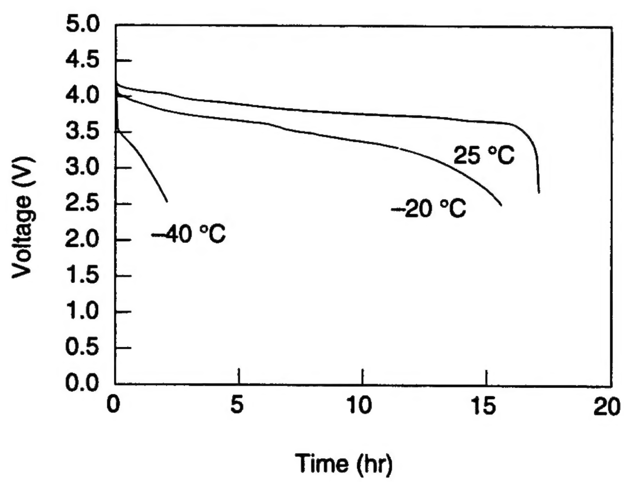


Figure 6. Typical discharge curves for cell III at constant current of 1 mA at various temperatures using 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC as electrolyte.

Conclusions

Ethyl methyl carbonate was found to be a useful cosolvent to increase the liquidus range of the $LiPF_6$ solutions in 1:1 EC-DMC at low temperatures. Thus, a 1.0-molar solution of $LiPF_6$ in 1:1:1 EC-DMC-EMC was found to possess good conductivity and electrochemical stability. Lithium and lithium-ion cells using the new electrolyte were found to be operable at temperatures down to –40 °C.

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